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13. ABSTRACT (Maximum 200 words)

Report developed under SBIR contract. This SBIR project has developed a low temperature polymer ceramic composite consisting of boron carbide layers bonded by cement, laminated with polymer sheets. The porosity of the ceramic was minimized by *in situ* hydrolysis of cement. The material has a layered structure designed to exploit the wear resistant properties of the ceramic and improve the toughness of the composite. The processing method is net shape, allowing large areas of material to be draped over forms for shaping prior to curing. The material is also easily cut to size before curing. Following curing the material is laminated with polymer sheets – a process which can be performed at temperatures as low as 150°C depending on the polymer used. The wear properties of the composite have been shown to compare favorably to those of partially sintered boron carbide. Applications for this material have been identified in several industrial settings including duct, chute and hopper linings. There is also a possible application as a satellite thermal control coating. Follow-on research would target several of these applications to identify the perceived weaknesses of current technologies and test the new composite in these capacities.

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Abstract

A low temperature polymer ceramic composite has been developed consisting of boron carbide layers bonded by cement laminate with polymer sheets. The material has a layered structure designed to exploit the wear resistant properties of the ceramic and improve the toughness of the composite. The processing method is net shape, allowing large areas of material to be draped over forms for shaping prior to curing. The material is also easily cut to size before curing. Following curing, the material is laminated with polymer sheets – a process which can be performed at temperatures as low as 150°C, depending on the polymer used. The wear properties of the composite have been shown to compare favorably to those of partially sintered boron carbide. Applications for this material have been identified in several industrial settings including duct, chute and hopper linings. There is also a possible application as a satellite thermal control coating. Follow-on research would target several of these applications to identify the perceived weaknesses of current technologies and test the new composite in these capacities. More basic research could be performed to explore the nature of the boron carbide cement bond.

1. INTRODUCTION

The Department of the Army Solicitation No. 96.2 requested research into biomimetic processes for the development of ultra thin polymer bonded composites containing hierarchical structure and improved mechanical properties.

A biomimetic process is a synthetic approach to imitate the natural formation of composites such as bones, teeth and shells. These natural composites consist of inorganic material such as calcium carbonate or hydroxyapatite embedded in polymeric proteins. The proteins are not merely a mechanical component of the composite but actually control and restrict the growth of the ceramic constituent. Although the formation of the crystalline ceramic particles is known to occur via hydrothermal processes, the processes by which the proteins control the ceramic growth are poorly understood. Nevertheless, the mechanical behavior of the natural composites is observed to be superior to the behavior of composites formed by mechanical mixing of the components. This improved behavior is generally attributed to the microstructure of the natural composites.

Hierarchical structures are ones in which basic structures are repeated over many length scales; a polymer matrix composite of continuous fibers in which each fiber is composed of a composite of smaller fibers embedded in a matrix. In contrast, a seashell is not hierarchical. It consists of calcium carbonate bricks joined by thin layers of proteinaceous material, shown schematically in Figure 1. The improved mechanical properties of seashell over calcium carbonate are due to the small size of the components; however, the mechanical behavior as a function of length scale has not been satisfactorily demonstrated. In other words, it is not known how small the constituent layers must be in order to realize improved properties. TPL proposed demonstrating the feasibility of a method for producing synthetic seashell consisting of materials with mechanical properties superior to those employed in seashells.

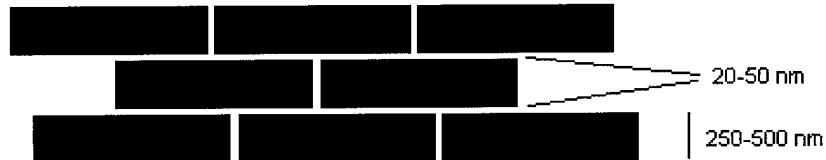


Figure 1. Schematic representation of nacre in which calcium carbonate 'bricks' are bonded together by thin layers of proteinaceous polymer

A composite consisting of boron carbide, cement and polymer was proposed as a synthetic analog of seashell in which thin layers of boron carbide bonded by cement were laminated with layers of polymer. The goals of the project were:

1. Demonstrate a low temperature method to produce dense (>95 vol %) boron carbide layers.
2. Demonstrate a strong adhesion between boron carbide and cement.
3. Demonstrate a boron carbide/polymer composite with high toughness.
4. Produce the composite at temperatures less than 300°C.

Most of these goals have been achieved and the feasibility of a low temperature processing method has been demonstrated. Boron carbide composites have been produced at temperatures of ~150°C. The composites are tough due to the incorporation of polymer and

wear resistant due to the presence of boron carbide. The strength of the boron carbide/cement bond appears adequate for some applications and may be improved through several avenues. The anticipated high volume fraction of ceramic in the composite has not been achieved. Although SEM imaging was performed, it was difficult to quantify because of particle pull-out during polishing. At this time, it is believed that the volume fraction of ceramic can not be increased to 95 vol%; however, this goal does not appear to be necessary for many tough, wear resistant structures.

The material that has been developed has wear properties comparable to those of a partially sintered boron carbide material. The new composite has some significant advantages over a sintered material. Boron carbide is sintered at temperatures of $\sim 2150^{\circ}\text{C}$ resulting in a partially dense ceramic (≤ 70 vol%). Full density can only be achieved by hot pressing at similar temperatures. The new material possesses a ceramic volume fraction of at least 70% at room temperature. The highest temperature required to manufacture the new composite is to melt infiltrate the polymer ($\sim 150^{\circ}\text{C}$). Large sheets of the new composite can be manufactured with no change in procedures. Further the composite can be formed and cut to size and shape prior to cement bonding similar to polyethylene sheets. Cement bonding of boron carbide is truly a net shape processing method. Consequently, large sheets of boron carbide composites can be made at relatively low cost with the most expensive component being the boron carbide powder. In comparison, large high temperature furnaces are difficult and costly to run. Typically hearth sizes are smaller than 12" in diameter. The boron carbide tends to shrink during densification; therefore, machining of the part is necessary after firing.

The new material is ideally suited for low-cost, wear resistant applications. These include, but are not limited to, hopper, duct and chute linings, pneumatic conveyor systems and dust collection systems. While none of these applications are high value, the volume of sales is substantial. In order to gain a market share, the cost/performance of the new material must be tested with respect to standard materials for each application. Another possible application for the material is as a thermal control coating for satellites. At this time, the exact requirements for this application are not known; however, interest in the composite was expressed by a NASA representative.

2. PROCESSING

Figure 2 is a processing flow chart visually describing the steps performed in the manufacture of the composites. The process is described briefly here and in greater detail below. Green tapes of boron carbide, cement and silica are cast and cut to size. The tapes are exposed to water to allow the cement to cure. The polymer binder originally added to the green tape is dissolved leaving only inorganic material. The cement bonded boron carbide sheets are allowed to cure to completion. Polymer sheets are placed between the boron carbide layers and the ensemble is heated in vacuum to $\sim 150^{\circ}\text{C}$ to allow the polymer to melt and infiltrate the boron carbide layers.

2.1 GREEN TAPE FABRICATION

Polypropylene carbonate (Aldrich, $M_w=50,000$) was dissolved in acetone to make a 25 wt% solution. Boron carbide (Cerac < 5 micron), cement (Nittetsu, colloidal) and silica (Cab-o-Sil, Cabot) were slowly added to the solution. The particles were suspended by ultrasound after each addition.

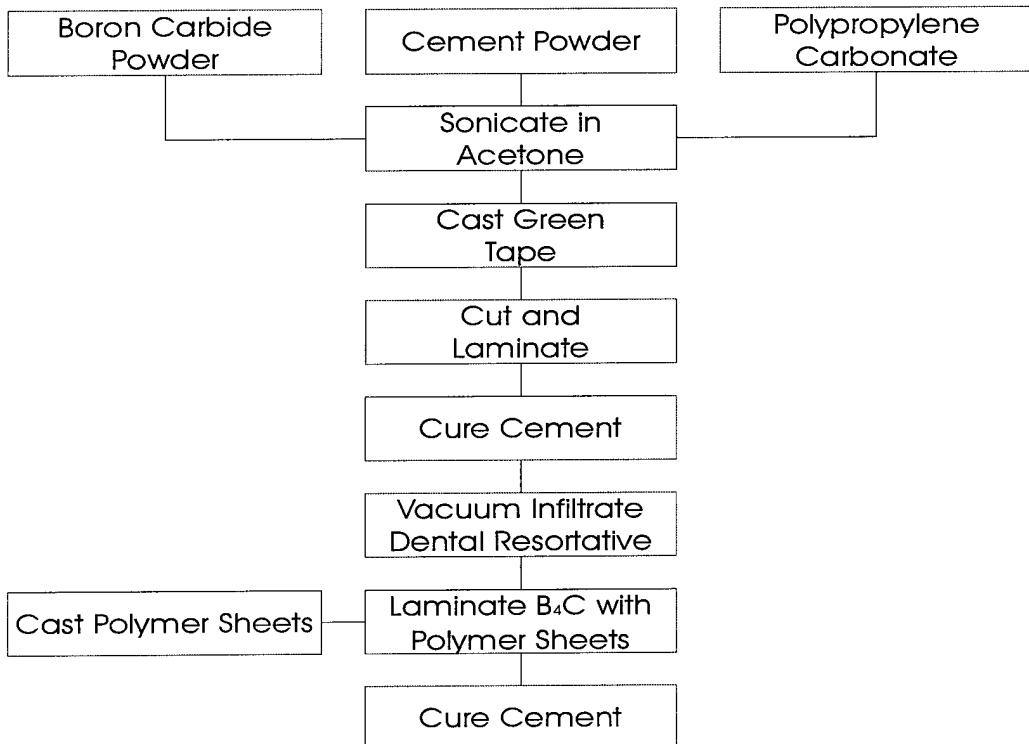


Figure 2. Processing flow chart showing steps to the manufacture of a low temperature boron carbide composite.

The boron carbide slurry was draw-cast on fluorinated polymer sheets, and showed excellent wetting and peel behavior. This material dried in about an hour under ambient conditions. The resulting green tape was 80% ceramic and had a 50/50 ratio of boron carbide to cementitious materials. The volume of cementitious material was high to promote more rapid cement curing of the boron carbide tapes but can be varied for various applications.

Although, the model system (nacre) consists of aragonite plates with thicknesses of approximately 0.5 microns, work by Aksay et al.¹ on partially sintered boron carbide sheets laminated with aluminum demonstrated that tough and strong composites could be obtained with layer thicknesses of \sim 100 microns. Tapes with thicknesses of approximately 100 microns were cast. Thinner sheets were also cast but became more difficult to handle. Similarly, thicker sheets could be prepared by lamination of boron carbide layers.

Lamination of the green tape was performed with a hydraulic press at loads of <5000 lbs. The green tape was cut into disks of 2 in. diameter suitable for wear testing or smaller rectangular samples (\sim 2 $\frac{1}{2}$ in. x $\frac{1}{2}$ in.) for infiltration studies.

3. BONDING OF BORON CARBIDE

The draw-cast tapes were formulated with dehydrated cement as well as silica. These two materials form calcium silicate hydrate upon exposure to water. The growth of CSH from

¹ A. J. Pyzik, I. A. Aksay and M. Sarikaya, "Microdesigning of Ceramic-Metal Composites," J. A. Pask and A. G. Evans, eds., *Ceramic Microstructures 86. Role of Interfaces*, 1986, 21 45-54.

these starting materials was expansive and filled pores between boron carbide particles. The sheets were placed in an incubator which maintained a temperature of 50°C at a relative humidity of 100%. (The elevated temperature was used to promote faster curing; however, samples have been cured at room temperature as well.)

The growth of CSH is a relatively slow process. Conventional cement sets in approximately one week and reaches full strength in a month. Nevertheless, cement growth was evident in approximately three days when the samples were removed, placed in acetone, dried and returned to the incubator. This step dissolved most of the polypropylene carbonate and allowed the cement to bond more freely to the boron carbide. Even after only three days, the samples could be handled without fear of breakage. Figure 3 shows a fracture surface of a cement bonded boron carbide sample. The angular particles are the boron carbide crystals and the needle-like particles are CSH.



Figure 3. Fracture surface of cement-bonded boron carbide sample. The acicular cement particles have been growing approximately one week.

4. COMPOSITE PROCESSING

Melt infiltration of cement-bonded boron carbide sheets was conducted with polypropylene and polyethylene. Polymer sheets were cut and sandwiched between boron carbide layers with a dead weight of 1 kg placed on top. The sandwich was placed in a vacuum chamber and heated to approximately 150°C. Infiltration and wetting behavior of the polymer into the boron carbide is excellent. The samples could be cut, sanded and polished. Figure 4 shows a cross-sectional image of a cement-bonded boron carbide composite infiltrated with polypropylene.

The layered boron carbide composite envisioned by TPL consists of alternating sheets of boron carbide and polymer. One goal of the proposal was to obtain a composite of 95 vol% ceramic. If the boron carbide sheets are cast at 100 microns in thickness, the polymer interlayers can only be approximately 5 microns thick (assuming the boron carbide layers achieve full density). A 5 micron thick polymer layer is a difficult goal to reach. Originally the boron carbide layers were laminated by polypropylene layers which were processed at TPL, Inc. These layers were quite thick, on the order of 1 mm. During melt processing, the polymer thickness was reduced to approximately 50 microns. The thickness of the polymer layers was



Figure 4. SEM cross-sectional image of cement bonded boron carbide composite.

reduced by starting with thin sheets of polyethylene (~60 microns). Although polymer layer thicknesses of 10 microns could be approached, thinner layers would be difficult. Figure 5 shows a low magnification SEM image of the composite indicating a fairly large polypropylene layer thicknesses. In addition, the boron carbide sheets were not fully dense.

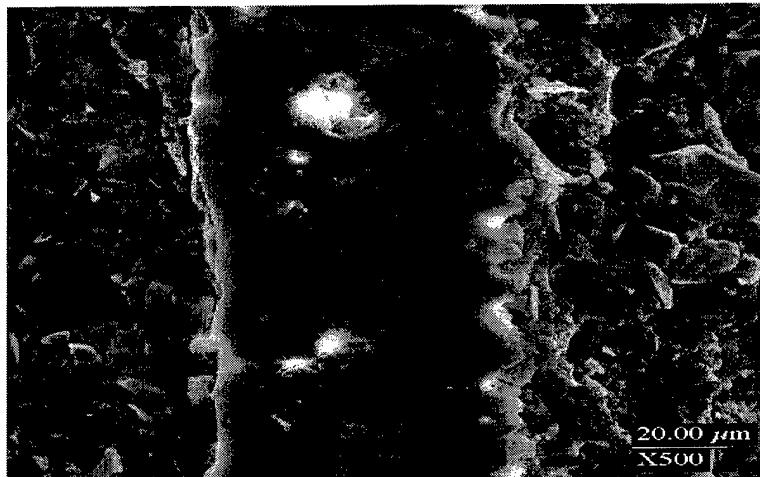


Figure 5. SEM image showing polypropylene layer thickness of approximately 60 microns.

5. MECHANICAL STRENGTH

The mechanical strength of the cement-bonded boron carbide layers was not quantified. Qualitatively, the sheets could be fractured by hand and were prone to breaking during processing. It is believed that this is a consequence of the bond between boron carbide and cement. An aggregate concrete consisting of cement, sand and stone is similar in nature to the cement boron carbide mixture, and, in fact, a thin sheet of concrete is quite weak in bending. Bonding between filler material and cement is known to be fairly weak. The strength of concrete is due to the continuous network of cement that forms around filler materials. In other words, the cement should not be thought of as a glue that connects strong boron carbide particles but rather as the load bearing material. In support of this argument, cracks have been observed around boron carbide particles in the cement network, see Figure 6. Since the

cement-bonded boron carbide consists of about 50% boron carbide, the cement network is not particularly robust. A reduction in the amount of boron carbide, however, might reduce the desirable wear properties.

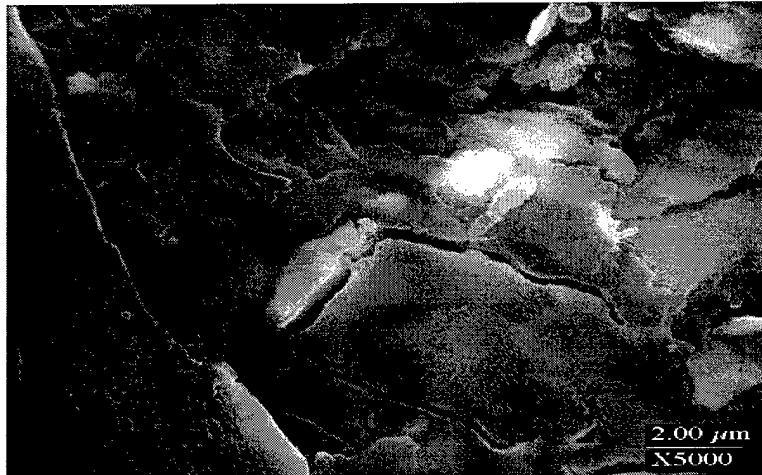


Figure 6. SEM image showing crack between boron carbide particle and cement.

6. WEAR TESTING

Wear tests of the composite material followed ASTM standard G99-90. This test describes a procedure for determining the wear of materials during sliding of a pin on a disk. The specimen to be tested is a disk 2 in. diameter (unspecified by the ASTM). The pin is a material with a hardness comparable to that of the sample to be tested. In our tests, stainless steel and zirconia pins were used with diameters of 3 mm and 0.8 mm respectively. The ASTM recommends a surface finish of 0.8 microns; however, in our tests the surfaces were left as processed. Wear can be determined by changes in dimension or changes in weight.

The cement bonded boron carbide composite was compared with boron carbide sheets which were partially sintered. The green ceramic was prepared by tape casting following procedures similar to those described above; however, the inorganic component of the slurry consisted solely of boron carbide. Sintering was performed in a graphite furnace under argon at 2150°C for 1 hour. The fired ceramic was approximately 70% of theoretical density. These specimens were purchased from Professor Ilhan Aksay of Princeton University.

Initial wear tests used a stainless steel pin on the sample. A load of was placed on the pin and the test was conducted for hours. Since no weight loss was measured for either the cement-bonded or sintered boron carbide disks, a harder material was sought for the pin. Small zirconia beads were obtained which were glued to the end of the steel pins. Although zirconia is considerably harder than stainless steel it is still much softer than boron carbide. The hardness of zirconia as measured by a Knoop indenter at a load of 100 g is 1200 compared with 2800 for boron carbide.

Two inch diameter disks were placed in the wear test apparatus. A load of 100 or 200 g was applied (221,000 or 442,000 Pa respectively). The samples were tested for 10 or 20 hours at a rotation speed of 88 rpm (3981 or 7962 m respectively). The results of the wear tests using zirconia pins are summarized in Table I.

TABLE I.
WEAR TEST RESULTS: ZIRCONIA PIN ON DISK

Sample	Change in Disk Weight	Change in Pin Weight	Change in Pin Length
B ₄ C Composite, 100 g load, 10 hours	0.0099 g	0.0005 g	0.05 mm
B ₄ C Composite, 200 g load, 20 hours	0.0035 g	0.0005 g	0.07 mm
Partially Sintered B ₄ C, 100 g load, 10 hours	0.0001 g	0.0001 g	0.02 mm
Partially Sintered B ₄ C, 200 g load, 20 hours	0.0000 g	0.0005 g	0.07 mm

In all cases, the wear track on the disk was only noticeable as a shiny region. Figure 7 shows the wear tracks on both samples observed at 500x magnification in an optical microscope. Magnified, the wear track of the composite shows some small grooves that are not present in the partially sintered material. The difference in track appearance may be indicative of a different wear process for the composite. Overall, the wear properties of the composite are roughly comparable to those of partially sintered boron carbide – without requiring high temperature firing.

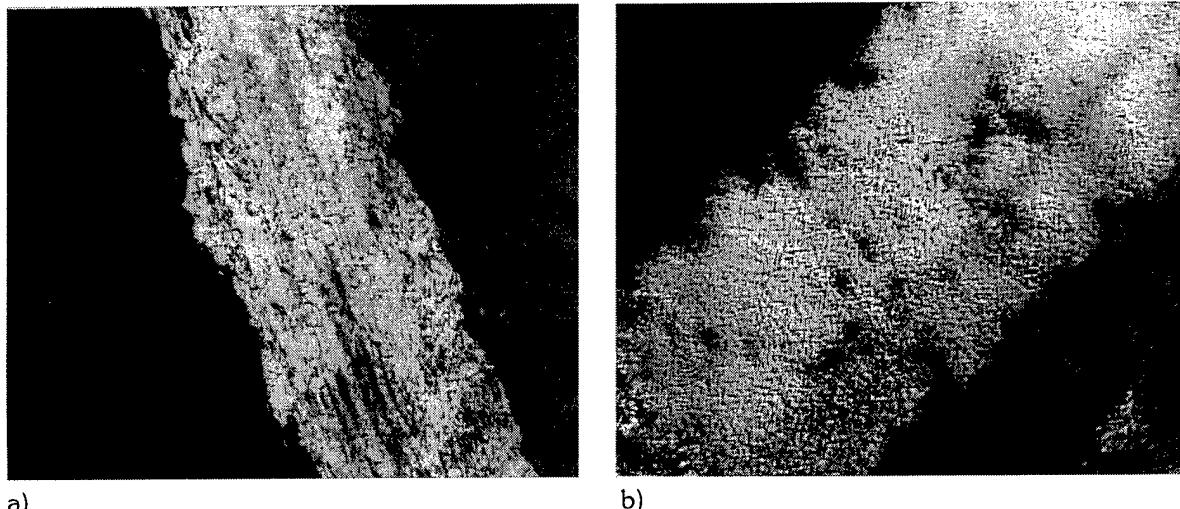


Figure 7. Optical micrograph of wear tracks on a) cement bonded boron carbide and b) partially sintered boron carbide. Samples were subjected to 20 hours of wear by a zirconia pin under a load of 200g.

7. APPLICATIONS

There are a wide variety of industrial applications for wear resistant materials each requiring its own material properties. Most applications are for linings over steel parts either to prevent product contamination, increase part lifetime or increase efficiency. In most cases, justification for the expense of a lining will only be considered if a significant increase in lifetime can be demonstrated such that the replacement cost of the steel part (often negligible) and the cost of downtime (often appreciable) are not exceeded. Slightly higher costs are considered only for applications which prevent product contamination if a significant improvement in the product can be realized. As a result, to be considered for an application, the new material must be low cost and be proven to increase part lifetime for each application to which it is directed.

Some of the material properties that are relevant to wear resistant linings in general are thermal shock, coefficient of friction, corrosion resistance, strength, toughness, hardness, weather resistance and electrical resistivity. Not all of these parameters are relevant to every application. In particular, the composite developed at TPL, Inc is not a high temperature material. Its current use temperature is slightly over 100°C, depending on the polymer used for lamination. It is quite possible that higher melting polymers could be utilized in the future, extending the operating range to over 200°C. Regarding the other material properties, few have been determined; however, certain assumptions can be made. The corrosion resistance of the material will most likely be dominated by the properties of the polymer; therefore, in terms of long term stability to chemicals and weather resistance the composite is likely to have properties similar to polyethylene. On the other hand, the coefficient of friction of the material will most likely be close to boron carbide; i.e., low. Although the individual cement-bonded boron carbide layers are not very strong, once laminated, the composite is fairly robust. In fact, the brittleness associated with ceramics is largely eliminated since the polymer seems to dominate this property as well. The hardness of the material is dominated by the ceramic as evidenced by the wear test data. The electrical resistivity of the material is unknown but, since the material is comprised of two insulators, it is expected to be high.

A partial list of applications for wear resistant linings (usually over steel) to which TPL's composite might be suited follows:

Mines, Mills, Smelters – hoppers, chutes, tanks, dust collection systems, ball mill scoops, ore car liners.

Cotton Seed Mills & Gins – conveyor screws, chutes, pipe elbows.

Grain Mills and Elevators – chutes, conveyor screws and troughs, hoppers and spouts, elevator heads, cyclones, pipe elbows.

Coal, Coke, Ash Handling – chutes, hoppers, ducts.

Pneumatic Conveying Systems – ducts, cyclones, dust collection systems, pneumatic cargo conveying systems.

Chemical and Plating Plants – tank lining, pipe elbows, fume and expeller stacks, conveyor screws.

Glass Plants – chutes, hoppers, conveyor tables.

Sand, Gravel, Crushed Rock Plants – spreader tables, pipes, chutes, hoppers, sand dryer lines, cyclones.

Cement, Concrete Plants – drag conveyors, chutes, ducts, hoppers, ball mill feeder chutes, air separators.

Clay Products Industry – hoppers, chutes, cyclones, pipe elbows, conveyor spouting.

Reclamation Projects – dredging operations.

The following is a list of competing technologies in these areas. These materials cover a wide range of material properties.

- ◆ Rubber plated steel-Abrasiplate, Linatex and Duothane
- ◆ Hardened steel (composite with chromium carbide)-Super-C
- ◆ Zirconia and alumina linings-ZAC and Durafax
- ◆ Ceramic composite-Ceramite
- ◆ Polyurethane linings-Kastalon

The composite developed at TPL is unique in this list. It has properties intermediate to these materials. As a result it could find use in one or more areas where it encompasses the right set of material properties for an application.

8. FUTURE RESEARCH

It is evident that more work must be done before cement-bonded boron carbide composites secure a place in the market. A composite with many useful properties has been demonstrated. Among these properties are high wear resistance and toughness achieved with a simple, low-cost fabrication technique. Ideally a number of tests need to be conducted including coefficient of friction (an instrument is currently being setup at TPL), strength and toughness. In order to meet specific application needs, different polymers might be used to alter the material properties. This type of work can proceed once a dialog has been set up with end users. These areas of research are relatively trivial. The area of greatest concern for the composite is the strength of the boron carbide cement bond. Although the composite may prove useful in its current state, further research could result in substantial enhancement of the boron carbide-cement bond strength.

Cement is a relatively poor material for structural applications. It is strong in compression but weak in most other loading geometries. In cement, filler is added to lessen the amount of cement used but the strength of the composite is due to the network of cement crystals that grow. In order to produce a strong ceramic by essentially gluing the ceramic together with an inorganic adhesive (cement), research should be focused on producing covalent bonding. Areas which could be studied to produce a strong cement ceramic bond are modification of the boron carbide surface chemistry and changes in the chemistry of the cement. Several routes to boron carbide surface modification have been identified, and the potential for rapid progress in this area is high.

9. CONCLUSIONS

The current research has demonstrated the feasibility of producing boron carbide polymer composites without firing of the material. Boron carbide particles are held in a cement network to form sheets which are laminated to form a tough, wear resistant composite by polymer layers. Processing of the composite is a net shape method and is flexible enough to allow complex geometries to be accessed. The wear properties of the composite compare favorably to those of partially sintered boron carbide. The wear resistant nature of the material combined with the ease and flexibility of the processing method suggest that the new composite may be ideal for many industrial applications. These include duct, chute and hopper linings. Follow-on research would target several of these applications to identify the liabilities of current technologies and identify the strengths of the new composite. More basic research could be performed to explore the nature of the boron carbide-cement bond.